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A Quantum Theoretical Study of Polyimides

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Final Report

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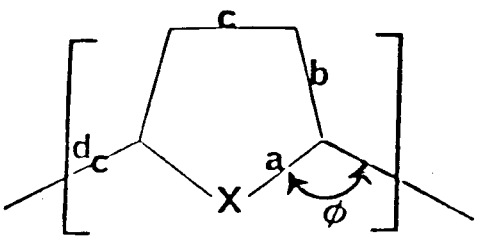
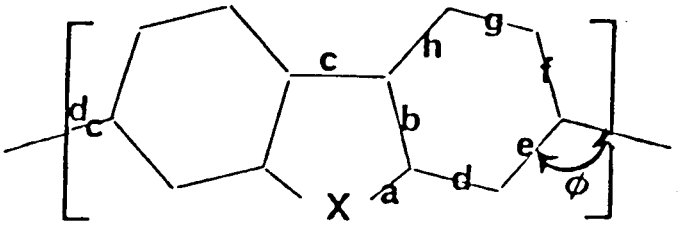
One of the most important contributions of Theoretical Chemistry is the correct prediction of properties of materials before any costly experimental work begins. This is especially true in the field of electrically conducting polymers. The object of this grant is to develop the Valence Effective Hamiltonian (VEH) technique for the calculation of the band structure of polymers. The band structure is needed in order to calculate properties such as ionization potential, spectra, and oxidation and reduction potentials.

The objects of the extension of one year to the grant are to develop the necessary VEH potentials for the sulphur and oxygen atoms within the particular molecular environments and to explore the explanation for the success of this approximate method in predicting the optical properties of conducting polymers. In the first six months of the continuation, potentials for the usual molecular environments for the oxygen atom have been developed. As for sulfur, it has been found that the model potentials need not include participation of d atomic orbitals for sulfoxide linkages (i.e. SO, SO_2) if only orbital energies (band structure in polymers) are needed.

Results of the study have been accepted for publication in the International Journal of Quantum Chemistry (Symposium), the Journal of Computational Chemistry, Chemical Physics Lettres, and have been submitted to the Journal of Chemical Physics. An example of the work so far is a comparison of the electronic structure of polymers obtained from two similar classes of

monomers. The unit cells of these two classes are the conjugated five-membered rings (IA-ID) and their dibenzo counterparts (IIA-IID).





Class I

IA, X=CH_2

IB, X=NH

IC, X=0

ID, X=S

Class II

IIA, X=CH_2

IIB, X=NH

IIC, X=0

IID, X=S

These polymers belong to a class where, upon doping, they are transformed from insulators to "organic" metals. In addition, the reduced dimensionality of polymers leads to characteristic optical, magnetic, and transport properties which differ from those of traditional semiconductors (4). Polymerization has been accomplished electrochemically for IB and, IC, and ID.

The reason for comparing these two classes comes from a peculiarity in the density of valence states diagram (DOVS) for monocyclic, conjugated polymers such as polypyrrole (IB).

As seen with many theoretical methods, the pi states near the Fermi level are dominated by contributions due to the inter-ring nonbonding states and show an extended, low binding energy shoulder due to the inter-ring bonding states. One state is nonbonding in the sense that the node passes near the inter-ring carbon-atoms, which link unit cells together, while the other pi state has a node passing through the heteroatom or the CH_2 unit. The inter-ring nonbonding state is represented by a flat band in the Brillouin zone due to the poor overlap between cells and thus by a larger peak in the DOVS. The wider band and concomitant lower absorption in the DOVS for the inter-ring bonding state is due to the larger atomic orbital coefficient on the bridge carbon, which thus gives greater overlap between cells. The effect of incorporating a dibenzo surrounding onto these monocyclic systems will be studied here.

The potential quantities derived from band structure calculations which are useful in the prediction of conductivity are the theoretical ionization potential (IP), band width of the highest pi band (BW) and the band gap (E_g); also, electron affinity (EA) can be calculated in the usual way as IP - E_g. These results are presented in Table 1.

In order to compare these theoretical results to the experimental values in Electrochemistry, oxidation (E_O) and reduction (E_R) potentials in volts versus the Saturated Calomel Electrode (SCE) have been calculated using relations 1 and 2.

$$E_O = IP - 6.3 \quad (1)$$

$$E = EA - 6.3 \quad (2)$$

These calculated values are also listed in Table 1. These relationships between theoretical quantities (given in eV) and experimental potentials (V.Vs. SCE) have been found to hold for the IP and E_g calculated by the VEH method for polyacetylene (PA), poly(p-phenylene) (PPP), IB and ID. These relations are quite close to those found by taking experimental values of gas phase IP and of the first optical transition for molecules.

The first observation of the results in Table 1 is the striking similarity of the IP and E_g for all dibenzo polymers. This similarity is in parallel with the similarity of structural parameters (unit cell length, inter-ring bond length, and the ϕ angle) and orbital coefficients (0.349 - 0.357) on the bridge C atoms for all dibenzo polymers. The results obtained by Bredas et al. for coplanar PPP are also listed in Table 1 and are remarkably similar to the results for dibenzo polymers. Thus, similarity among all dibenzo polymers may be rationalized in terms of orbital interactions.

The nodal characteristics of the highest occupied band in Class II are similar to Class I polymers, i.e., there is a node passing through the central atom (X or the CH_2 unit). In a first order approximation, the central atom would have no contribution to the IP and the monomers of Class II polymers can be thought of as rigid biphenyls giving coplanar PPP.

Similarly, the C atoms of Class I can be considered as cis-transoid PA backbone. The spread in IP for Class I (whether experimental or due to the particular parameterization chosen)

is attributed to a second order effect of the heteroatom on the bridge C atoms. The effect on the pi system is expected to be greater in Class I than in Class II due to the relatively fewer number of carbon atoms (4 to 12 in a unit cell).

It has been suggested that since ID and cis-PA can be n-doped by Na naphthalide while IB cannot be, the E_R of IB must be more negative than 2.9 V (25). The lower E_R (-4.3 V) or IB may be due to the above discussed second effect. According to our calculations, the dibenzo polymers all should be n dopable by Na naphthalide.

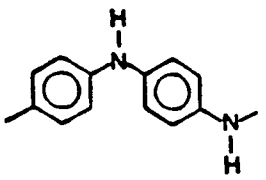
Table 1 Calculated band width (BW), ionization potential (IP), band gap (E_g), electron affinity (EA), oxidation potential (E_0), and reduction potential (E_R). The values of E_0 and E_R are with respect to Saturated Calomel Electrode (SCE). All units are in eV or Volts.

Polymer	BW	IP	E_g	EA	E_0	E_R
IA	4.3	6.3	1.4	4.9	0.0	-1.4
IB	3.8	5.8	3.8	2.0	-0.5	-4.3
IC	4.1	6.0	2.7	3.3	-0.3	-3.0
ID	4.5	7.0	1.8	5.2	0.7	-1.1
cis-PA	6.5	6.6	1.3	5.3	0.3	-1.0
IIA	1.7	7.2	3.0	4.2	0.9	-2.1
IIB	0.9	7.1	3.2	3.9	0.8	-2.4
IIC	1.6	7.2	3.2	4.0	0.9	-2.3
IID	1.0	7.4	3.1	4.3	1.1	-2.0
PPP	1.9	7.4	3.2	4.2	1.1	-2.1

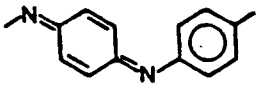
Much interest in oxidized polyaniline (PAn) has been shown recently since the protonated form has a high electrical conductivity (~10 S cm^{-1}). What sets polyaniline apart from other conducting polymers is that its highest conductivity is obtained at an intermediate level of electrochemical oxidation and that it becomes insulating again at a higher potential. Chemical analysis of the highest-conducting oxidized PAn which was put in contact with acid showed that one out of every two nitrogen atoms can be protonated.

Oxidation introduces a "quinoid" form into a ring by dehydrogenating two amine N atoms to the imine form. We use the convention, due to MacDiarmid, of designating the non-protonated forms by the letter A and the forms that have been put in contact with protonic acids (~ pH 0) by the letter S. The oxidation states are designated by the number 1 for the reduced (original) form of PAn and 2 for the idealized form where all N atoms are oxidized, introducing one quinoid ring for every benzenoid ring. Thus, the half-oxidized PAn (form 1½ A) would have one pair of imine N atoms and one pair of amine N atoms in the idealized unit cell and protonation of the imine lone pairs would give the highest conducting 1½ S form, polyemeraldine.

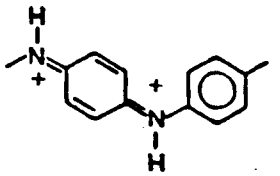
The proposed mechanisms of charge transport have varied from band transport based on the number of spins per protonation level to a mechanism involving molecular excitons based on agreement between CNDO/S calculations on proposed structures



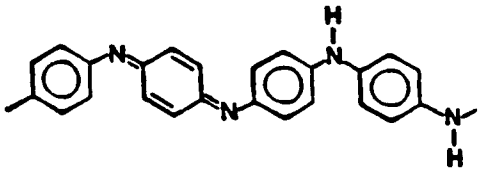
1A



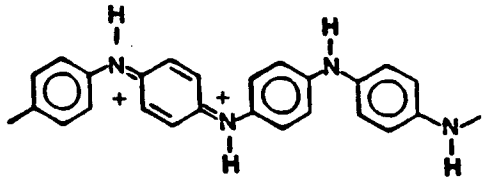
2A



2S



$1\frac{1}{2}$A



$1\frac{1}{2}$S

and photoelectron spectra. In studies of the effect of temperature on conductivity a variable range hopping mechanism has been proposed. However, non-quantitative results are obtained by application of the model. The structure of PAn or "aniline black" is ill-characterized but studies of aniline oligomers with well-defined numbers of oxidized units have shown octomers to have properties almost identical with those of the quasi-infinite polymer.

Some authors have studied the problem theoretically by optimizing the geometry of various aniline oligomers with standard molecular orbital methods such as the MNDO method and using the geometries for the unit cells in band structure calculations on the various oxidized and protonated states of PAn. Valid optical transitions for molecules and polymers are calculated with the Valence Effective Hamiltonian method (vide infra).

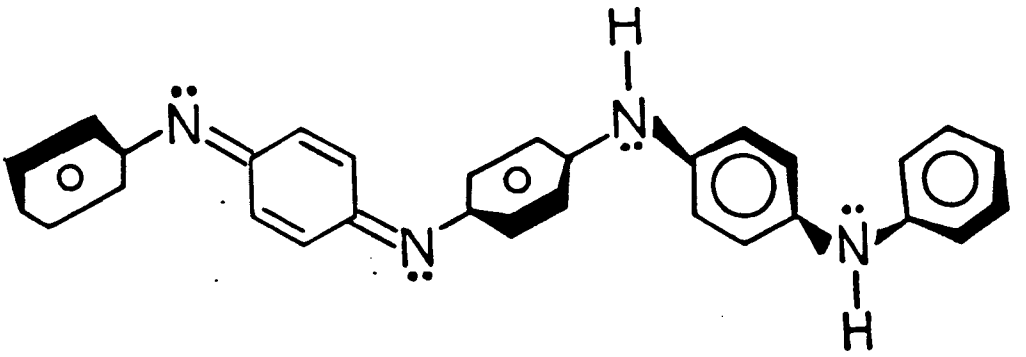
If band structure calculations on 2A, 2S, 1½A, or 1½S are performed using standard quinoid and aromatic bond lengths and angles (or those from small oligomers such as N,N' diphenyl diiminoquinone), the lowest conduction (unoccupied) band, LCB, is characterized as being localized on the quinoid π system, while the highest valence (occupied) band, HVB, consists of the aromatic π system and the N lone pair in the unprotonated cases. The band gaps, E_g, are 1.2 and 1.3eV for 2A and 2S and 1.3 and 1.4eV for 1½A and 1½S, which are close to the band edge of the first optical transistion (1.4eV) for the oxidized but nonprotonated forms of PAn.

If the MNDO optimized geometries are used from oligomers of sufficient length, the quinoid group remains localized in I but diprotonation of I produces a structure II where the quinoid "defect" is delocalized over the central three rings and the "quinoid" rings are skewed out of the zig-zag plane of the N atoms. This is in contrast with I where quinoid defect is localized in one ring which remains in-plane. C_i symmetry resulted for II where the central ring has four bonds of length 1.46Å and two of 1.36Å and is ~20° out of plane. The next rings on either side have four lengths of 1.44Å and two of 1.37Å are skewed ~40° from the central ring. The CN bond lengths are 1.34, 1.38, 1.35, and 1.43, respectively from the middle.

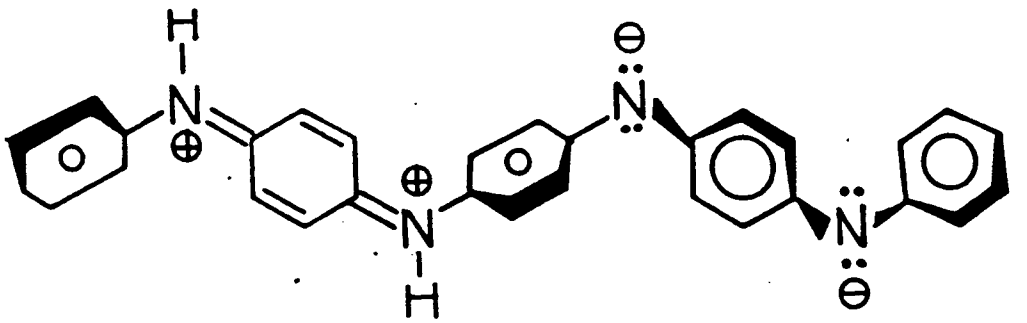
Assuming similar delocalizations in 1½S as in the interior of II, the unit cell for 1½S can be reduced to two C_6H_4NH units with the geometries found for the central and neighboring unit in II. The E_g in this case is reduced to 0.3eV.

In 1½A there is a high barrier to displacement of the quinoid moiety in the 1½A form due to nonequivalent N and NH groups (see figure 1). At one point it must pass through a zwitterionic structure which is much higher in energy. The 1½S form has all NH groups and thus displacement of a quinoid group involves an equivalent structure.

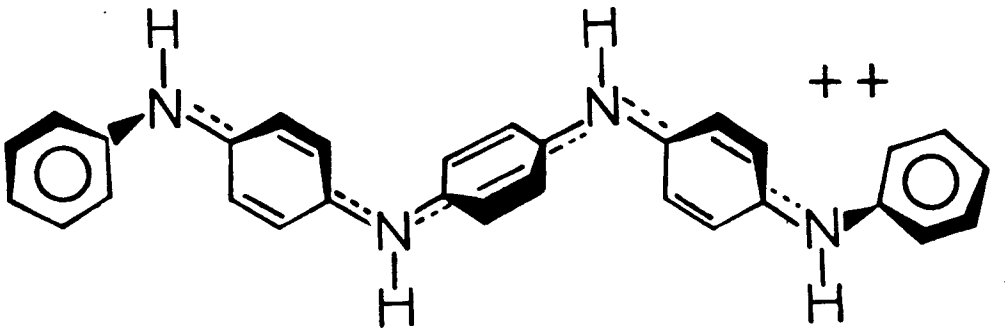
In order to have an idea of the barrier height that a zwitterionic intermediate would have in 1½A, MNDO calculations were carried out on molecule I' where the bond angles and



I



I′



II

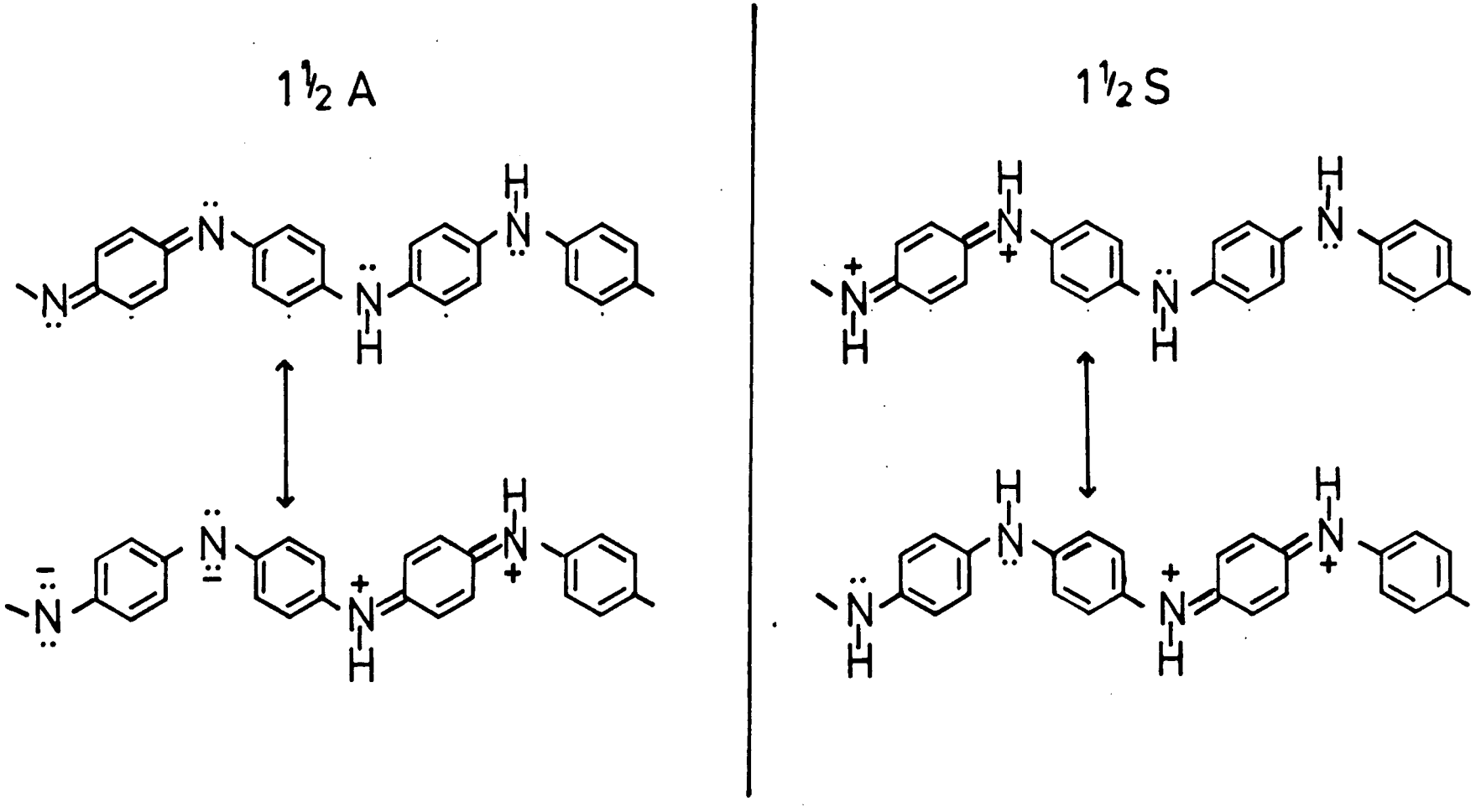
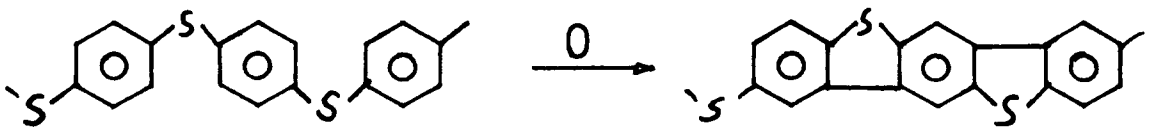


Figure 1 (Left) Structures for 1½A including the zwitterionic structure (Bottom) after displacement of the quinoid center over two rings. (Right) Equivalent structures for 1½S after displacement of the quinoid centre over two rings.

dihedral angles were optimized but where the corresponding quinoid and benzenoid bond lengths were held fixed. The zwitterionic I' form was found to be 6.1eV higher in energy than I.

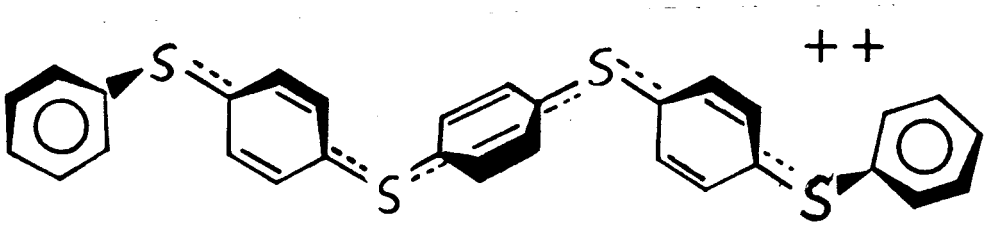
Thus, the role of protonation for increasing the conductivity of half-oxidized PAn is to equivalence the coordination number of the N atoms (thus, their oxidation states). In eliminating the zwitterionic species and delocalizing the defect the mobility of the transport is greatly increased.

Similar quinoid-benzenoid results were found for oligomers of polyphenylene sulfide (PPS). PPS can be thought of as an isoelectron analog of PAn where the NH group is replaced by an S atom. At high dopant levels the electrical conductivity of PPS is greater than $1S^{-1}cm^{-1}$ but only at the expense of extensive chemical modification of the polymer chain.



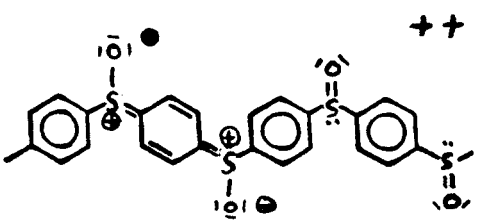
At low dopant levels there is no chemical modification of the polymer and conductivities are as high as $0.1S^{-1}cm^{-1}$, depending on dopant concentration. From studies on oligomers, oxidation by the dopant introduces a quinoid defect which is delocalized over several rings, as in PAn. Contrary to PAn,

oxidized PPS does not need protonation to equivalence the coordination number of the atoms connecting the rings.



VEH calculations on half-oxidized PPS gave a band gap of 0.4eV, quite close to the value for 1½S PAn (0.3eV). VEH calculations on sulfoxide linkages were also carried out and gave a band gap of 0.4eV. Sulfoxide geometries are not well calculated by the MNDO method; so PPS geometries with experimental dimethyl sulfoxide geometries were employed.

The sulfoxide linkage also provides for a quinoid structure upon oxidation of the ring system. This is not the case for sulfone linkages. Thus, sulfone linkages are expected to lower intrinsic conductivities in polymers where the quinoid-benzenoid mechanism predominates.



It is of particular note that the VEH method, which is a parameterized method of ab initio quality, gives much better agreement with experiment for properties such as band gap than does the ab initio Hartree-Fock method itself. In the VEH case band structure calculations are based on quantities borrowed from model clusters and assumed to be transferable.

In the VEH method Fock matrix elements F_{pq}^{j} for functions p and q are calculated as the sum of a kinetic energy integral and the potential energy element which is represented by weighted sums of projection operators over the basis functions p and q in cells 0 and j:

$$F_{pq}^{j} = \langle {}^{0}_{p} | T | {}^{j}_{q} \rangle + \sum_{h} \sum_{A} \sum_{l} \sum_{m} \sum_{t} C^{A}_{lmt} \langle {}^{0}_{p} | {}^{Ah}_{lmt} \rangle \langle {}^{Ah}_{lmt} | {}^{j}_{q} \rangle$$

This expression has rapid convergence properties; the kinetic term decays nearly exponentially with distance between function p centered in cell 0 and q in cell j; the formally infinite summation over h is rapidly stopped due to the multiplication of the overlap terms which, themselves, decrease exponentially.

The fact that the VEH method uses systems of limited extention (compared with ab initio methods where the two-electron terms are of much slower decay) corresponds to introducing an effective screening of the bare Coulombic potential which leads to better agreement with experiment for band gaps.

This effect has been estimated by J. Delhalle of Namur, Belgium in a detailed analysis of the analytic and asymptotic properties of the Fock density matrix in the LCAO representation

(J. Chem. Phys. 85, 5286 (1986)). At the Fermi level the HF density of states (DOS) vanishes due to the combination of two effects: the discontinuity in the population function which disrupts the analytical behavior of some k-dependent density matrix elements, and also the long-range nature of the Coulomb interactions. They combine into slowly decaying trigonometric series which vary quickly near the k points where the population function of the bands drops from 2 to 0.